
Tufa sedimentation in changing hydrological conditions: the River Mesa (Spain)

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| A B S T R A C T |

The processes controlling tufa deposition along the River Mesa (NE Spain) were studied from April 2003 to September 2009, based on six-monthly monitoring of physical and chemical parameters of the river water and sedimentological characteristics, including deposition rates on tablets. With a mean annual discharge around 1.5m³/s, the sedimentation rate (mean 2mm/yr) recorded important spatial, seasonal and interannual variations. The river waters are of the calcium bicarbonate type. In this study, three distinct river stretches were distinguished based on the steady groundwater inputs, some of low-thermal nature. Groundwater discharges controlled the water chemical composition, and some sedimentation features too. At each stretch, an increase in pCO₂ and conductivity was measured around the spring sites. Decreasing trends in conductivity or alkalinity with high enough saturation values with respect to calcite were only clearly observed in the intermediate stretch, which had higher tufa deposition rates than the other two. Tufa deposition rates were higher in cool (autumn+winter) than in warm (spring+summer) periods. In some low-rainfall warm periods, tufa deposition was inhibited or limited due to the low flow –mainly from groundwater inputs– and to the dryness of some river sites, which indeed favoured erosion during flooding. A decrease in yearly deposition rates from April 2006 onwards paralleled an important reduction in the river discharge. Groundwater inputs, drought periods and flood events should therefore be considered to understand fluvial tufa sedimentation in semi-arid conditions.

KEYWORDS | Recent fluvial tufas. Deposition rates. Hydrochemistry. Hydrological variability. Continental Mediterranean climate.

INTRODUCTION

Fluvial tufa deposition is associated with meteoric waters that discharge from karstic systems in carbonate areas (Ford and Pedley, 1996; Pentecost, 1996; Arenas *et al.*, 2010). Present-day tufa depositional dynamics in fluvial systems has been a matter intensively studied from different perspectives for the last 25 years (Lorah

and Herman, 1988; Chafetz *et al.*, 1991; Liu *et al.*, 1995; Drysdale and Gillieson, 1997; Kano *et al.*, 2003; Kawai *et al.*, 2006; Shiraishi *et al.*, 2008; Vázquez-Urbez *et al.*, 2010, 2011). The studies are focussed on different cases that cover varying climate conditions, including temperate climate in Germany (Merz-Preiß and Riding, 1999; Arp *et al.*, 2001) and Japan (Kano *et al.*, 2003; Kawai *et al.*, 2009; Hori *et al.*, 2009), alpine climate in Croatia (Emeis *et al.*, 1987;

Lojen *et al.*, 2004), high altitude alpine climate in China (Liu *et al.*, 1995; Lu *et al.*, 2000; Yoshimura *et al.*, 2004), seasonally wet tropical climate in Australia (Drysdale and Gillieson, 1997) and continental Mediterranean climate in Spain (Ordóñez *et al.*, 2005; Pedley, 2009; Vázquez-Urbez *et al.*, 2010).

Most of the studied fluvial systems with tufa deposition are fed by small spring discharges at the headwaters, with limited or no groundwater inputs along their courses, and hydrological conditions are barely considered to be of great influence on the sedimentation characteristics. In streams with small-discharge springs a seasonal pattern of discharge parallel to rainfall distribution is observed when karstic aquifers have short water residence periods (Hori *et al.*, 2009; Kawai *et al.*, 2009). On the other hand, when rivers are strongly influenced by long-term groundwater inputs, discharge shows slight seasonal variations both in the river (Vázquez-Urbez *et al.*, 2010) and in the springs (Jacobson and Usdowski, 1975). Many present tufa systems with steady water discharge usually show a seasonal pattern in sedimentation rates and sediment geochemical composition (Matsuoka *et al.*, 2001; Kano *et al.*, 2003; Kawai *et al.*, 2006; Shiraishi *et al.*, 2008; Hori *et al.*, 2009; Arenas *et al.*, 2010; Vázquez-Urbez *et al.*, 2010, 2011). For example, the River Piedra, in the Iberian Range (NE Spain), is a tufa system in continental Mediterranean climate that fits the aforementioned statements, with a steady annual discharge (1.22m³/s) and a seasonal pattern in tufa deposition and geochemistry (Arenas *et al.*, 2010; Vázquez-Urbez *et al.*, 2010, 2011).

The River Mesa is another tufa-depositing river in the Iberian Range, also in a climatic context with marked seasonal variability. The present river has a low-gradient longitudinal profile with distinct sedimentary characteristics. The mean annual discharge is around 1.5m³/s, similar to other tufa-depositing rivers (*e.g.*, the nearby River Piedra, Vázquez-Urbez *et al.*, 2010). However, the River Mesa as great hydrological variability (including pluriannual drought and frequent flooding events) and receives constant low-thermal groundwater inputs. This all makes this river a suitable scenario to assess the influence of a more complex water discharge pattern on tufa deposition characteristics.

Six-monthly monitoring of the River Mesa in a total of 16 sites covering the different environmental sedimentary settings was carried out over 6.5 years (April 2003 to September 2009) to obtain data on i) hydrochemistry and ii) tufa sedimentation on artificial substrates. The purpose of this study was to discuss the factors that control the recent tufa dynamics of a high-discharge fluvial carbonate system characterized by i) wide hydrological variability through space and time, and ii) an anomalous behaviour with respect to the expected pattern of seasonal carbonate deposition.

THE STUDIED AREA

The River Mesa valley (Fig. 1) is located in the central sector of the Iberian Range, a NE-SW trending alpine intraplate mountain chain, and in the southern sector of the Tertiary Almazán basin (NE Spain). From headwaters to mouth the river passes across Triassic sandstones, dolostones and gypsum, Jurassic and Cretaceous limestones and dolostones and Miocene conglomerates, sandstones and mudstones (Vera, 2004). Jurassic and Cretaceous rocks hold the regional aquifer that feeds most rivers in that area (Servicio Geológico de Obras Públicas, 1990; Lunar *et al.*, 2002). Impressive Pleistocene and Holocene tufa outcrops are common along the River Mesa valley (Vázquez-Urbez, 2008; Vázquez-Urbez *et al.*, 2012), which account for significant fluvial tufa deposition in the past.

The River Mesa is an indirect tributary of the River Ebro (Fig. 1). It flows along 50km with a general northeast trend. The surface of the drainage basin is 622km² and the altitude ranges between 1518m (Aragoncillo Massif) and 690m (La Tranquera reservoir). We studied the lower reach of the River Mesa, about 30km long, between Mochales and La Tranquera reservoir. In this stretch, the river width varies from 3 to 8m and its longitudinal profile has a mean slope of 1.05%. Some gentle knickpoints exist near Algar and Calmarza villages (Fig. 2).

The climate in the River Mesa area is of continental-Mediterranean type with strong seasonal contrasts (Fig. 3). Data supplied by meteorological stations (see Fig. 3) indicate a mean annual air temperature of 13°C and a mean annual precipitation of 410mm over the period 2003-2009. There is a strong thermometric contrast, with mean values of 4.5°C in December and January and 23.3°C in July. Annual precipitation was irregularly distributed with maxima in May (60mm) and October (52mm).

Recent mean discharge (last twenty years) of the River Mesa reaches 49hm³/year, although it shows a marked variability (data from the Confederación Hidrográfica del Ebro, Spain; see Figure 2 for location of the gauging station). From 2003 to 2009, higher discharge events took place during spring (mean 1.92m³/s in May) whereas lower ones were recorded in summer (1.01m³/s in August). Flood events surpassing 20m³/s were frequent in spring. In many months, a remarkable decrease below 1m³/s in water discharge was observed (Fig. 4). Total discharge includes low-thermal groundwater inputs near the village of Jaraba. According to the data supplied by Pinuaga-Espejel *et al.* (2004) the mean discharge from those springs is 570-650L/s. This feature is constant throughout the year. During some

summer months, most water of the River Mesa stemmed from these low-thermal springs in Jaraba; upstream of Jaraba, some parts of the river remained dry, in particular in drought periods. Commonly, this circumstance was noticed between Calmarza and Jaraba during field work.

METHODS

Along the River Mesa a total of 16 sites were chosen for periodic (six-monthly) monitoring of physical and chemical parameters from April 2003 to September 2009. These sites were selected according to depositional settings, topographical features, points of water discharge and flora associations (Figs. 1; 2). Tufa sedimentation rates were measured and water and sediment characteristics were studied in every site.

Sedimentation rate monitoring

Limestone tablets (25x15x2cm) were installed in different subenvironments along the River Mesa (Fig. 2), lying parallel to the floor. From April 2003 to September 2006, 15 sites were monitored along the river. Due to the similar results from some sites and the loss of tablets in other ones, from October 2006 to September 2009, the number of monitored sites was reduced to 10, including a new tablet, *i.e.*, tablet 7 (Table I, Electronic Appendix, available at www.geologica-acta.com).

The tablets were removed at the end of the warm periods (spring and summer) and cool ones (autumn and winter). The tablets were first air-dried for 5 days. After that, the amount of sediment accumulated on each tablet was measured by means of a micro-erosion metre based

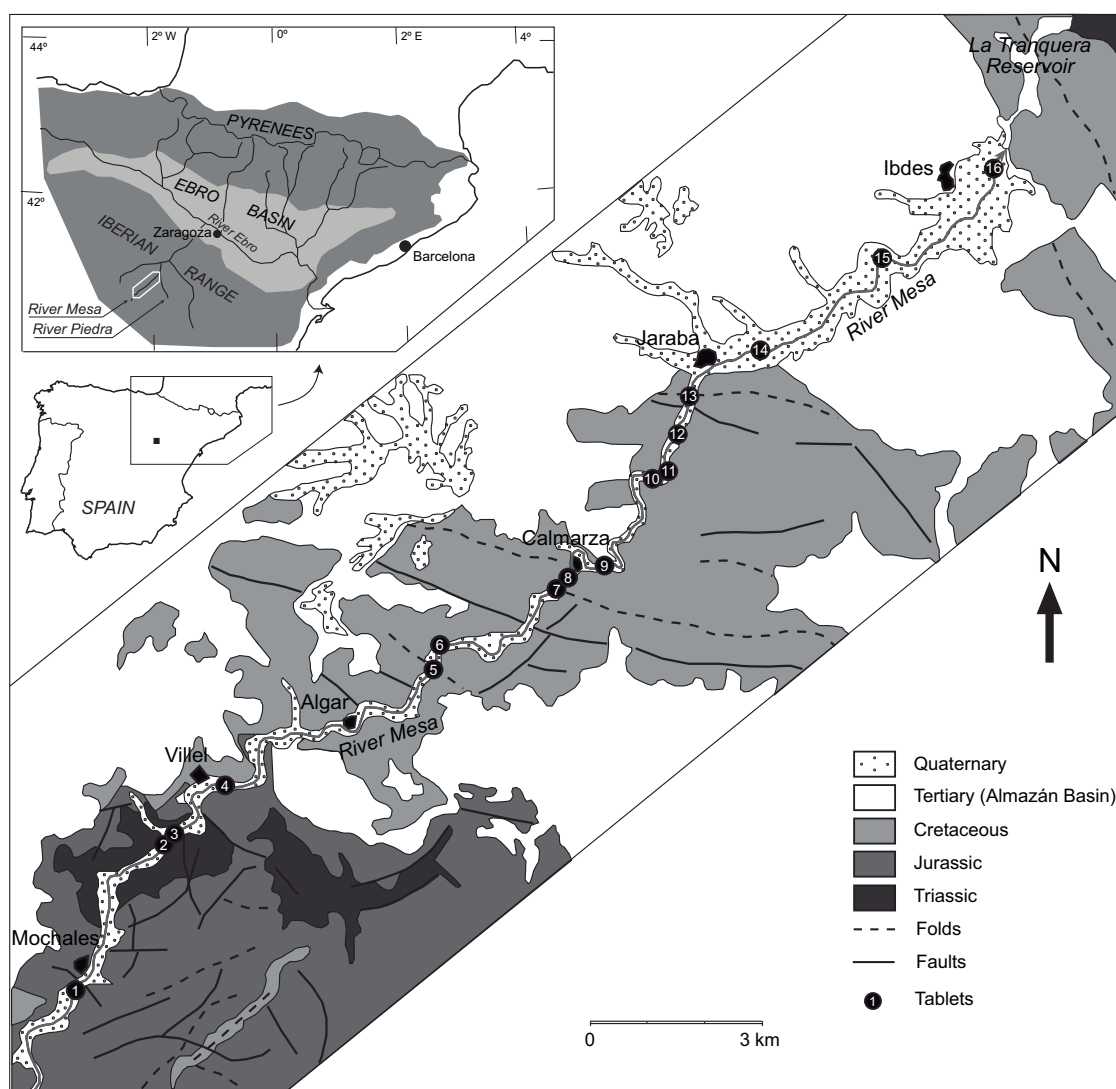


FIGURE 1 | Location and geological setting of the lower valley of the Mesa River. Location of tablets is indicated.

on that designed by Drysdale and Gillieson (1997). About a week after their removal, the tablets were put back in their original position.

The differences in sediment height (mean of the 50 points per tablet) between two consecutive measurements represented the six-month sedimentation rates at each site (Table I).

Flow dynamics, water sampling and analyses

Water depth and water flow velocity were measured at all sites four times a year (at the end of the four seasons). Flow velocity was measured by a surface velocity meter.

Water samples for chemical analysis were taken along the River Mesa at points with tablets (Figure 2). Sampling was made bianually at the end of June and December, from June 2003 to June 2009. The results are shown in Table I. Conductivity, temperature and pH were measured on-site using a Jenway 4200 portable conductivity meter and an Orion 250A pH meter. Upon return to the laboratory, samples were filtered for cation analysis using a 0.45µm Millipore cellulose filter acidified with ultra-pure HNO₃ to pH<2. Alkalinity was analyzed within 24 h of sampling by volumetric titration with 0.05 N HCl. Cl⁻ was determined by ion selective electrode (ISE) analysis, and SO₄²⁻ by a modification of the Nemeth colorimetric method (Nemeth, 1963), usually within 3 days. Cations were analysed in the filtered and acidified samples: Ca²⁺, Mg²⁺ and Na⁺ by atomic absorption spectrophotometry and K⁺ by flame photometry. Analytical errors were less than 2% for alkalinity, less than 3% for Ca²⁺, Mg²⁺, Na⁺ and the anion determinations, and less than 7% for K⁺. In the present study the percentage of charge imbalance for the analytical data was always <10%.

Speciation-solubility calculations to obtain calcite saturation index (SI_c), total dissolved inorganic carbon (TDIC) and partial pressure of CO₂ values of water samples were performed with the PHREEQC code (Parkhurst and Appelo, 1999) and the WATEQ4F thermodynamic database (Ball and Nordstrom, 2001) supplied with it.

Sediment sampling: mineralogy and texture

Carbonate sediment was sampled in situ from the tufa surface at several field settings every 6 months, in the middle of the warm and the cool periods (from June 2003 to June 2009). At the laboratory the most recent contributions of each period were picked. These were ground and sieved to a size of 53µm prior to X-ray analyses. X-ray diffraction was performed with a Phillips PW 1729 diffractometer (equipped with a graphite monochromator, using CuKα radiation and operating at 40K and 40mA with a step of 0.040° 2θ) at the Crystallography and Mineralogy Division of the University of Zaragoza (Spain).

Textural observations of the six-month deposits (sediment sampled from the tablets at the time of thickness measurement) were made using a stereomicroscope and by scanning electron microscopy (JEOL JSM 6400, Servicios de Apoyo a la Investigación, SAI, of the University of Zaragoza).

SEDIMENTARY CHARACTERISTICS OF THE RIVER MESA Tufa SYSTEM

The morphological and compositional (lithological and biological) features of the fluvial bed along with some physical flow characteristics (water velocity and depth) of

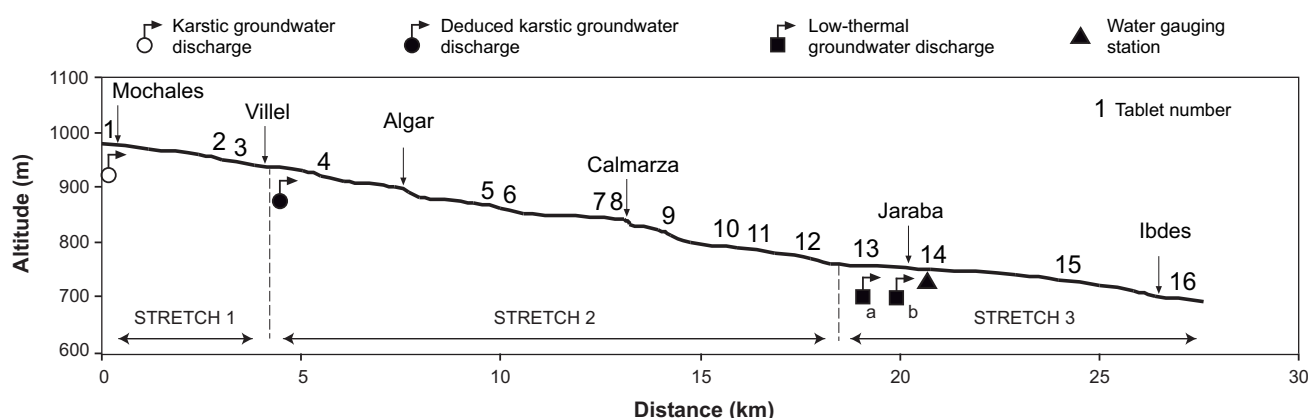


FIGURE 2 | Longitudinal profile and location of tablets in the River Mesa. The three stretches differentiated in this work are indicated. Point a in the third stretch corresponds to the situation of Huerta de la Hoz spring and point b to the situation of Las Pilas and San Luis springs.

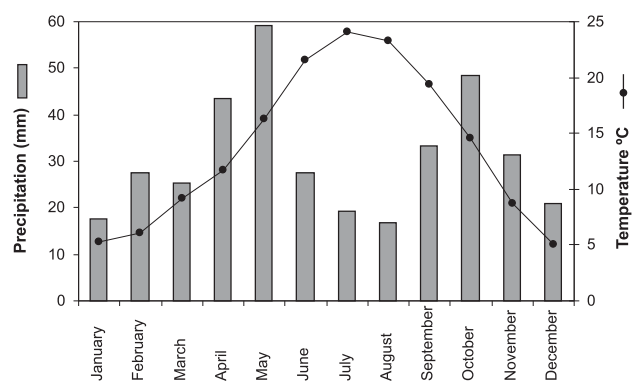


FIGURE 3 | Mean monthly precipitation and temperature from 2003 to 2009. Data from Milmarcos, Ateca, Alhama de Aragón and La Trancquera meteorological stations (data provided by the Agencia Estatal de Meteorología, Spain).

the River Mesa allowed to distinguish four main fluvial subenvironments, in which distinct facies formed (Table I). Textural and structural characteristics of the carbonate sediments deposited on tablets, along with the types of the related floral substrates allowed, distinguishing the following carbonate facies to be differentiated:

i) Facies A: Filamentous algae (macroscopic) lying parallel to the floor, associated with cyanobacterial and moss mats and diatoms (Fig. 5A, C, D), which generally constituted extensive deposits, covering a great part of the river bed for some tens of meters (Fig. 5B). These components were poorly to moderately coated or impregnated by calcite and constituted a porous fabric. Some detrital, primarily tufaceous grains were trapped by algae. This facies was common in many parts of the riverbed, as compared to facies B and C. It formed in small, generally stepped jumps, rapids, subhorizontal platforms and irregular horizontal beds with cobbles. In these sites, mean six-month water velocity mostly ranged from 70 to 110cm/s, and depth from 9 to 25cm (Fig. 5B). On four occasions, water flow velocity was lower (*i.e.*, 50–60cm/s).

In the Scanning Electron Microscope (SEM), the sediment consisted of filamentous algae and mosses (Fig. 6A–D) irregularly coated by spar and micrite calcite crystals of varied shapes and sizes (Fig. 6D), that may form clumps up to 0.24mm long. These may include a variety of diatoms and calcified filamentous cyanobacteria, which also appeared adhered to the filamentous algae and mosses (Fig. 6D). No clear seasonal microtextural differences were observed.

ii) Facies B: Laminated carbonate deposits (stromatolites) and calcified microbial mats, which made up dense and hard deposits, commonly of lateral extent limited to some parts of the river bed (*e.g.*, discontinuous areas decimeter to 1–2m wide and long) (Fig. 5E, F). These formed in small jumps,

rapids and subhorizontal floors and, less commonly, in irregular horizontal beds with cobbles, in which six-monthly mean water flow velocity varied from 70 to 120cm/s and depth from 10 to 15cm, exceptionally 25cm (Fig. 5F).

This facies consisted of laminae (0.5 to 3mm thick) mostly formed of calcite tubes (Fig. 6E, F); calcified cyanobacterial filaments, mucilaginous substance, bacterial rods and cocci bodies as well as diatoms appeared associated (Fig. 6G). The tubes evoke the growth of calcite around decayed cyanobacteria (in some cases *Phormidium*). These cyanobacterial tubes can be arranged as sheet-like palisades, as coalescent hemi-domes or at random; in some cases, the height of the tubes represents the thickness of a single lamina. The spaces among tubes are occupied by spar and micrite calcite as well as by other microbial components (*e.g.*, filamentous cyanobacteria, diatoms, mucilaginous substances and unidentified bacteria).

The inner diameter of the tubes can be either 0.5 to 3µm or 5 to 6µm; the coating thickness is up to about 2µm and 9µm, respectively (Fig. 6G). In some cases, the thicker coatings are found in sediments of cool periods. Calcite crystals of the tubes can be varied in size and shape, and neither of these two features seem to present clear seasonal differences.

iii) Facies C: Very thin, discontinuous (patchy) deposits made of sparse filamentous algae and mosses, diatoms, microbial, mostly cyanobacterial films, some molluscs, insect nests and annelid tubes (Fig. 5G, I, K). Commonly, carbonate sediment both coating these components or among them is poor. This facies formed in sites consisting of gravelly and cobbly beds influenced by groundwater inputs. At the monitored sites, six-monthly mean water velocity ranged from 60 to 120cm/s and depth between 10 and 30cm (Fig. 5H, J, L).

Carbonate sediment appeared as clumps of calcite irregularly and patchily distributed on algal filaments and mosses. The sediment among these was almost absent. Both spar and micrite calcite were present (Fig. 6H).

iv) Facies D: Loose lime mud with clays and fine to very coarse sand-size, allochthonous and autochthonous carbonate grains (Fig. 5M). This facies constituted massive deposits formed in slow flowing and dammed areas upstream of small stepped jumps (Fig. 5N), and generally the thicker accumulation formed during flood events. Mean six-monthly water velocity was very slow (27 to 35cm/s) and depth ranged between 25 and 45cm, with a minimum of 0 and a maximum of 52cm.

In most cases, facies A and B were associated laterally, so that both could appear on the same tablet at the same time,

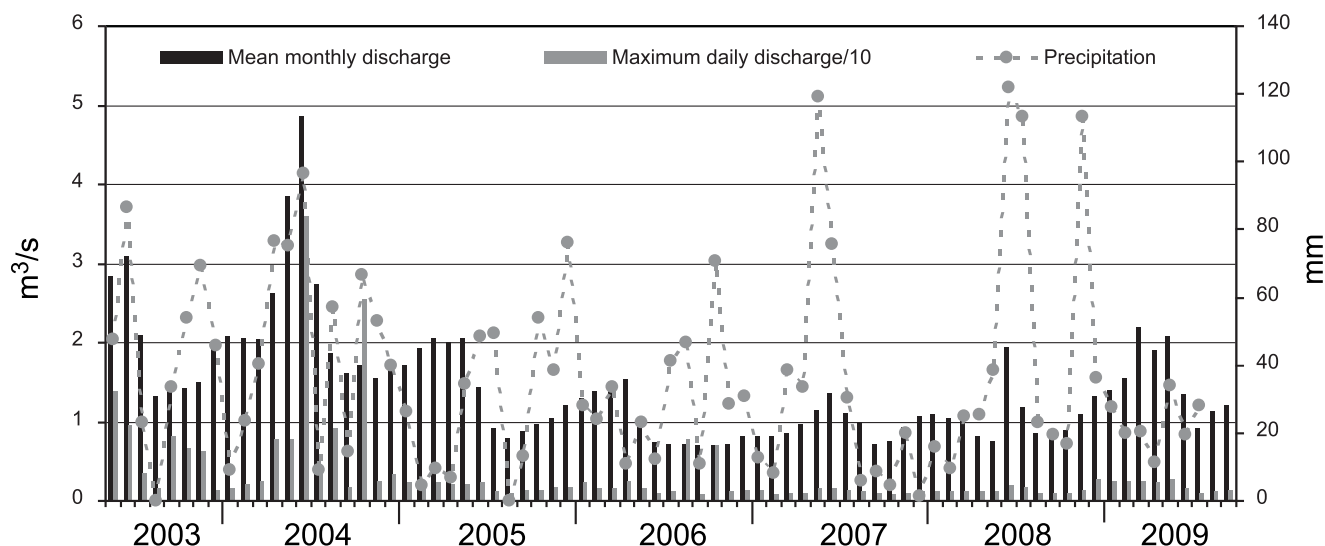


FIGURE 4 | Mean monthly discharge and some extreme flood events from 2003 to 2009. Monthly precipitation from 2003 to 2009. Discharge data from a gauging point 700m downstream of Jaraba (data provided by the Ebro Hydrographic Survey, Spain). Meteorological data from Milmarcos, Ateca, Alhama de Aragón and La Tranquera stations (data provided by Agencia Estatal de Meteorología, Spain).

although one was dominant in each environment. In other cases, one facies was replaced with the other, which became dominant over time. That seems to be related to changes in environmental conditions, *i.e.*, in water flow velocity and/or depth. For instance, facies B preferentially formed in shallower conditions than facies A. Facies A seemed to be more liable to erosion during flooding or high flow conditions (*e.g.*, high discharge events in spring and summer).

HYDROCHEMISTRY

Hydrochemical characters of the river water

Water chemistry along the course of the River Mesa is shown in Table II (Electronic Appendix, available at www.geologica-acta.com) and the profiles of major parameters (conductivity, water temperature, alkalinity, calcium, pH and chloride contents, as well as calculated total inorganic carbon, partial pressure of CO₂ and calcite saturation index) are summarized in Figure 7. The River Mesa waters are of bicarbonate-calcium type with pH values mostly between 7 and 8.7. Conductivity shows a wide variation (between 555 and 876 $\mu\text{S}/\text{cm}$) and the contents of the dissolved components related to the carbonate system were relatively constant: alkalinity values mostly between

250 and 300 mg/L, calcium between 70 and 90 mg/L and magnesium between 20 and 30 mg/L.

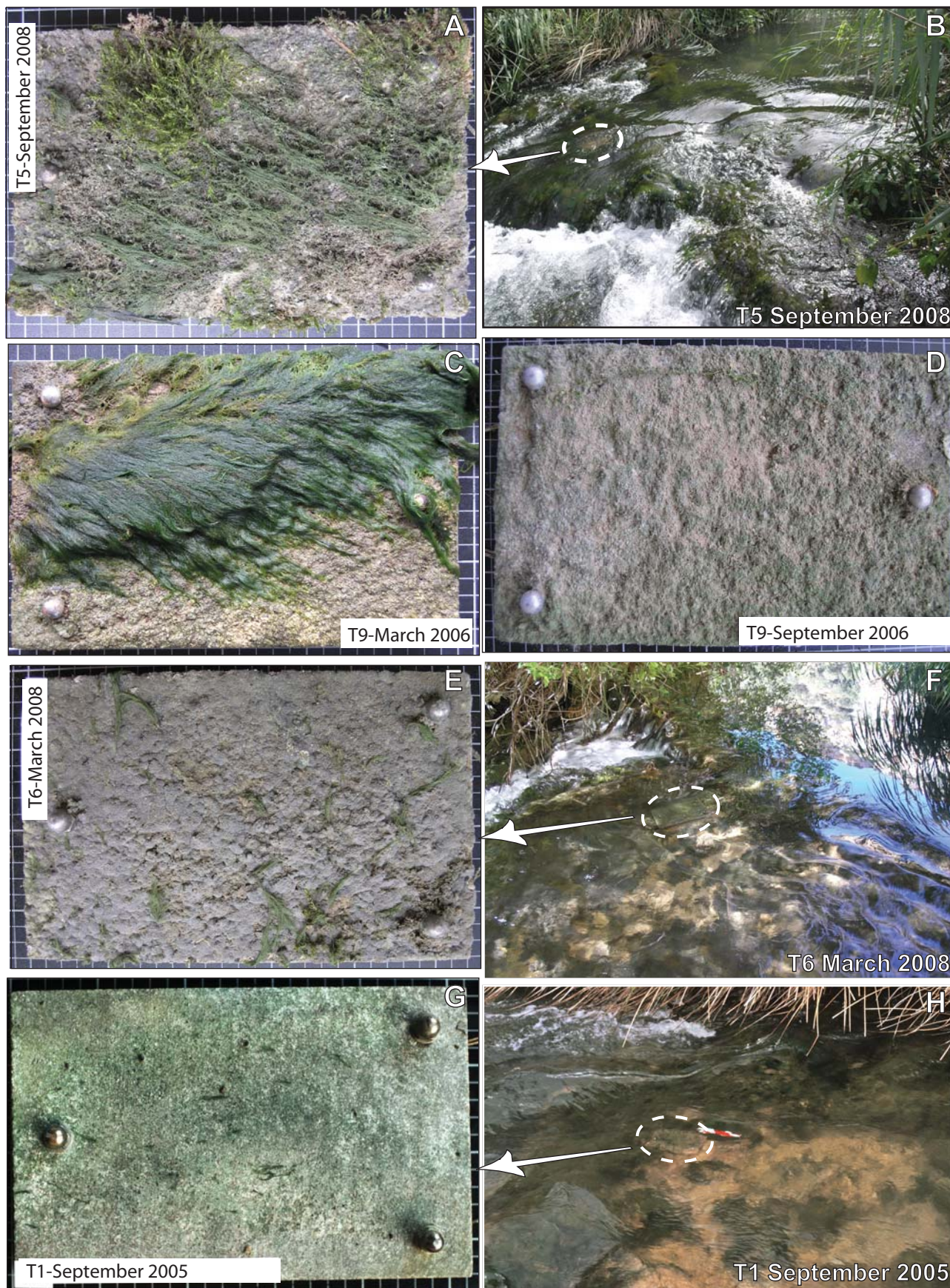
Overall spatial and temporal hydrochemical trends

From the spatial evolution of the hydrochemical parameters (Fig. 7) during the monitored period, the studied section of the River Mesa can be divided into three different stretches (Figs. 2; 7):

Stretch 1 (from point 1 to point 3) mainly characterized by an overall seasonal pattern in most of the measured parameters at point 1 (Fig. 2), as it occurs in similar tufa-precipitating streams (*e.g.*, Kano *et al.*, 2003; Kawai *et al.*, 2006). These parameters evolved with non-systematic increasing or decreasing trends along the stretch. Overall downstream decreasing values could be observed for alkalinity, TDIC and log pCO₂ (Fig. 7B, E, F), whereas overall increasing trends were observed for the SI_c values (Fig. 7G). Calcium contents usually decreased between points 2 and 3 (Fig. 7C), suggesting that tufa sedimentation mainly occurred at the end of this stretch.

Stretch 2 (from point 4 to point 12) began with a clear jump in all the hydrochemical parameters at point 4. These jumps brought out the influence of

FIGURE 5 | Views of sedimentary facies on tablets and subenvironments in the field. A, B) Facies A at site 5 (small stepped jump) in September 2008. C, D) Facies A at site 9 (irregular gravel bed) in March and September 2006. Notice the erosion of the algal mass in D). E, F) Facies B at site 6 (sub-horizontal platform) in March 2008. G, H) Facies C (sparse) at site 1 (gravel bed) in September 2005. I, J) Facies C at site 4 (gravel and cobble bed) in September 2005. Notice thin mass of poorly coated filamentous algae that trapped fine detritals. K, L) Facies C (only gastropods on a microbial film) at site 13 (gravel bed close to spring upstream of Jaraba village) in March 2005. M, N) Facies D (clay and lime mud) at site 12 in September 2006 (dried floor). Grid in left column images is 1x1cm. All tablets are 25x15cm.



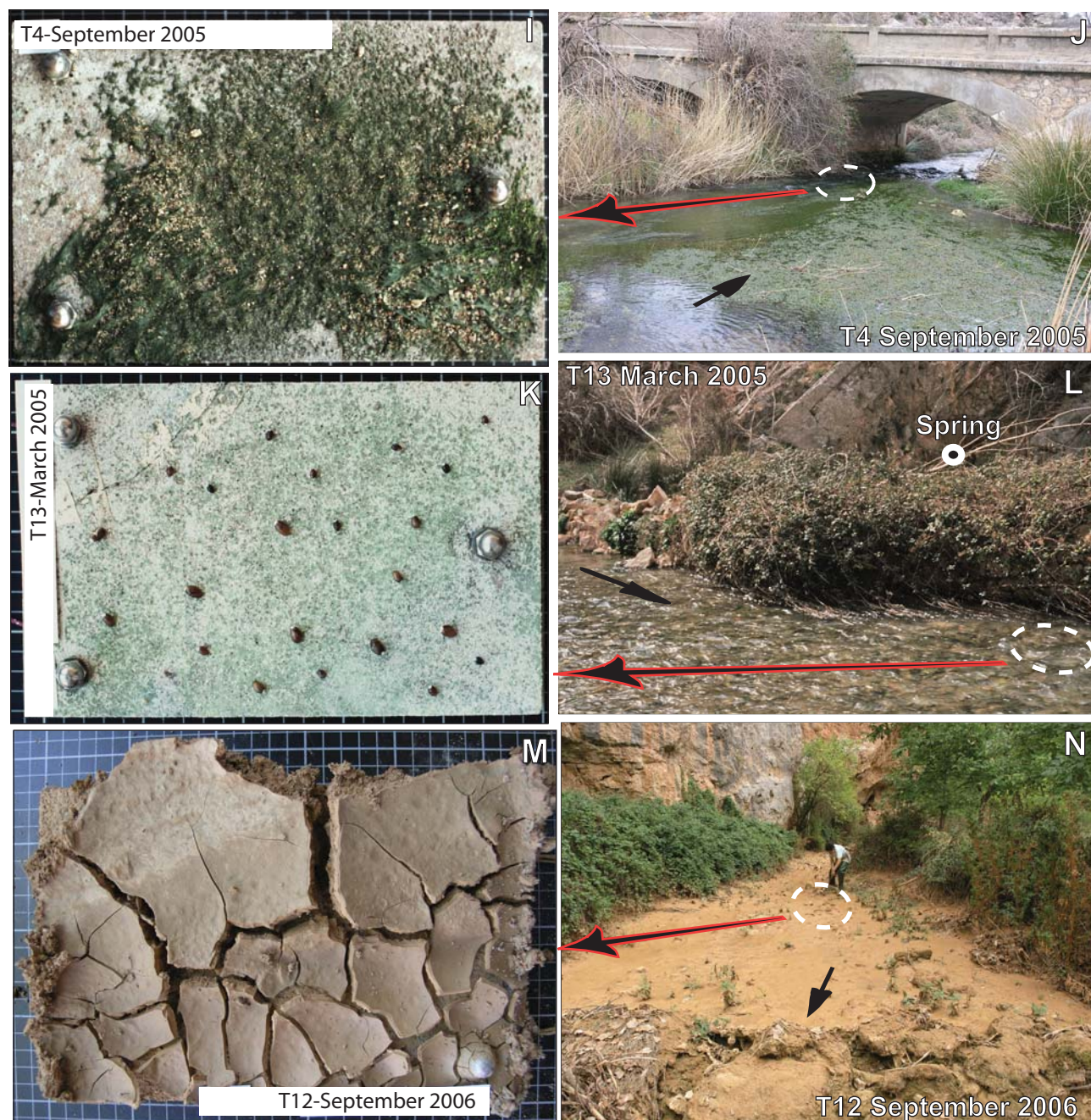


FIGURE 5 | Continued.

groundwater inputs between points 3 and 4. This stretch was characterized by much clearer and continuous downstream decreasing trends in conductivity, alkalinity and TDIC values (Fig. 7A, B, E). Calcium concentrations also clearly decreased from June 2003 to June 2006. From January 2007 to January 2009 (coinciding with the period of low discharge in the River Mesa; Fig. 3) the calcium decreasing trend was obscured, although net reduction in calcium concentrations were usually observed between points 4 and 12 (Fig. 7C). The

SIc, always with positive values (Fig. 7G), showed a relatively stable behaviour, especially in cool periods. Overall, those trends would be consistent with a more generalized carbonate precipitation in this stretch.

Stretch 3 (from point 13 to point 16) was characterised by the input of the Jaraba thermal waters around point 13. This input drastically changed the trends observed upstream (e.g., temperature, conductivity, alkalinity, TDIC, pCO_2 , calcium, pH and SIc values of the river waters; Fig. 7).

In contrast to the upstream stretches, most parameters (*e.g.*, conductivity, alkalinity, Ca^{2+} and TDIC) showed no significant downstream changes along stretch 3, which suggests additional groundwater inputs along it. Only log pCO_2 decreased from point 13 downstream. The SIc first increased, then remained constant through space (Fig. 7F). All these trends would not support the existence of important tufa sedimentation except, perhaps, at the end of the stretch (points 15 and 16, about 6 and 10 kilometres downstream from Jaraba springs; Fig. 2), where some decreasing trends in calcium contents were observed (Fig. 7C).

Water temperature showed a pattern reflecting seasonal changes in air temperature. Point 1 showed a moderate seasonal amplitude (with a temperature difference lower than 4.5°C ; Fig. 7H) buffered by the “still subterranean” character of the river waters, near a spring feeding the River Mesa. From point 1 to point 12 water temperature increased in summer and decreased in winter downstream.

From point 12 downstream, low-thermal water discharges in the River Mesa drastically changed the temperature trend of the river waters. Measured temperature at the emergence of a thermal spring, some 10 meters away from point 13, was rather constant through time (20.8°C ; Table 1 and Auqué *et al.*, 2009). Sampling point 13 recorded the mixing effects between river and thermal waters. Therefore, temperature at this point also showed a moderate seasonal variation, with values between 13.2 and 19.2°C . From point 13, river water temperatures increased slightly even in the cold periods supporting the existence of additional thermal water discharges downstream of that point. Only at the final downstream sampling point 16 a decrease in temperature was observed.

From June 2003 to December 2004, Cl^- and Na^+ concentrations were lower than 60 y 30mg/L , respectively; but from June 2005 to January 2008 (the drought period), the dissolved amounts of these elements showed a twofold increase (Table II); from January 2008, the Cl^- and Na^+ concentrations tended to decrease towards the initial values (chloride trends are shown in Fig. 7I). The conductivity values, reflecting the Total Dissolved Solids (TDS), also mimicked this trend (Table II). The period with the highest Cl^- , Na^+ and conductivity values matched up with the lowest measured discharges in the River Mesa. The rest of the parameters (mainly those from the carbonate system) did not show this temporal trend so clearly along the whole examined section of the River Mesa, although the highest values of alkalinity, TDIC, Ca^{2+} , and SIc values in the second stretch were measured during that drought period, probably reflecting the low tufa sedimentation in that period.

Hydrochemical effects of the Jaraba thermal discharges

The Jaraba springs belong to one of the main thermal systems in the Aragón region and, at present, there are three thermal resorts and several mineral water bottling plants in the area. The temperature (between 20 and 32°C) and compositional characters of the thermal springs (Table 1) display a certain spatial variability. However, temperature values and compositional characters of springs showing the highest temperatures (*e.g.*, Las Pilas spring; Table 1) are constant through time. The spatial variability of temperature and chemical composition is due to the existence of mixing processes (Tena *et al.*, 1995; Pinuaga-Espejel *et al.*, 2004; Auqué *et al.*, 2009) between deep thermal groundwaters and shallow, cooler waters at the emergence of the Jaraba springs.

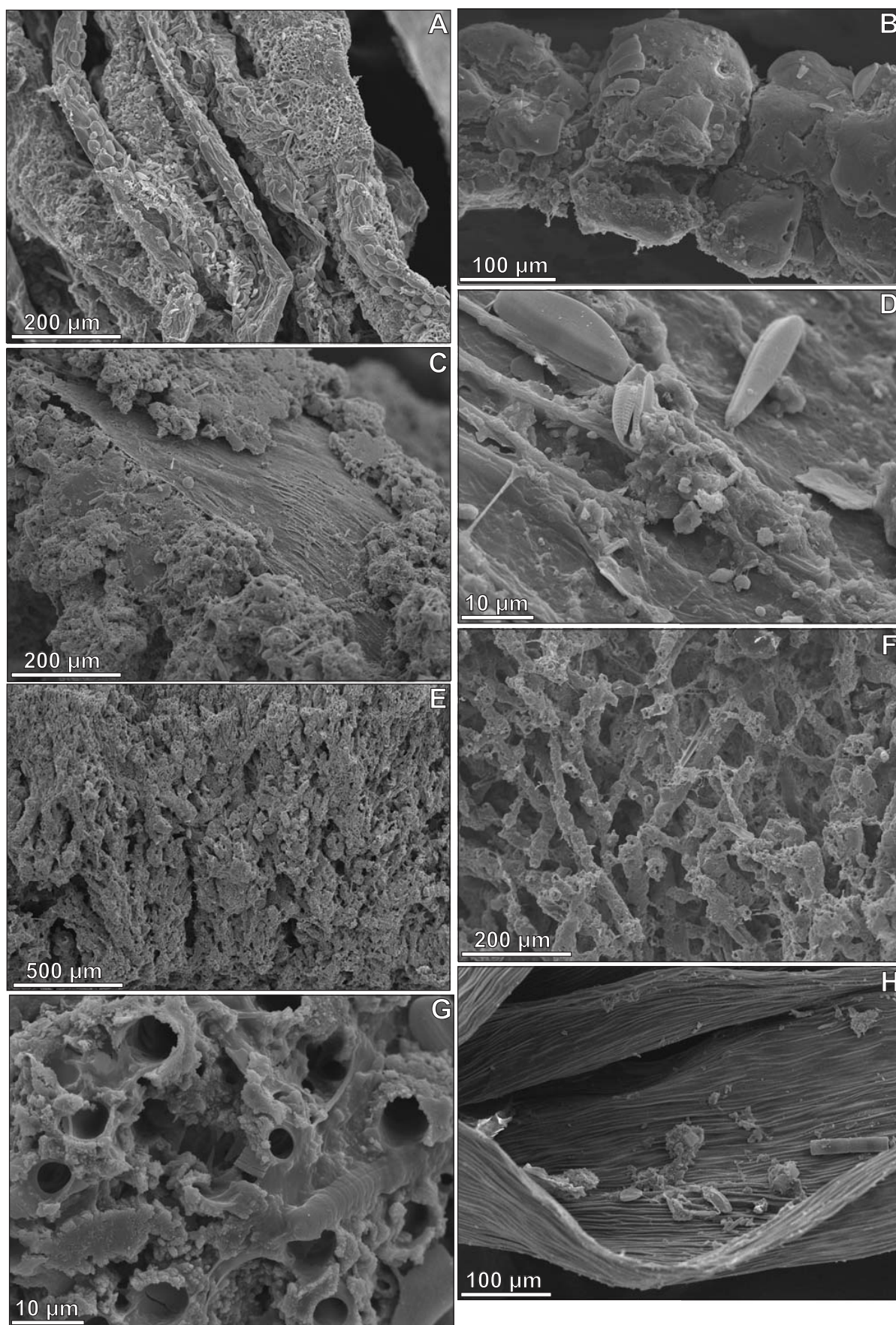
The contribution of such thermal waters to the flow of the River Mesa (between 570 and 647L/s ; Pinuaga-Espejel *et al.*, 2004) is high enough to drastically change the chemical characters of the River Mesa waters downstream of point 13 (Figs. 2; 7). The thermal waters discharging at point 13 (Huerta de la Hoz spring) display a temperature of 21°C (Table 1), consistent with the measured temperatures in the river at this point.

Most of the thermal springs at Jaraba are in equilibrium or near equilibrium with respect to calcite and show higher pCO_2 and alkalinity contents and lower pH values than the river waters upstream of point 12. All these characters are consistent with the abrupt changes in these parameters observed at point 13. The existence of additional thermal discharges downstream (as indicated by the temperature trends; Fig. 7H) probably promote the increasing and/or irregular trends in conductivity, alkalinity and calcium values which suggest low carbonate precipitation along this stretch (see below).

SEDIMENTATION RATES

The sedimentation rates of the tablets installed along the River Mesa (Fig. 2) and main environmental characteristics of each site are shown in Table I.

As mentioned above, the studied part of the River Mesa can be separated into three stretches conditioned by the presence of springs (*e.g.*, upstream of site 1 and 4 and between sites 12 and 14; see Figs. 2; 7). The characteristics of the sediment (coarse allochthonous detritals with sparse carbonate deposits versus tufa facies) also varied through these stretches (Table I). At sites where gravel bedforms dominated, the sediment (tablets 1, 13, 15 and 16) consisted of less than 0.25mm/y (except for one case with 1.09) of



detritals and gastropods, minor algae and microbial films. The monitoring of these sites spanned from April 2003 to September 2006.

Stretch 1, comprising tablets 1 to 3, included a long way almost without carbonate deposition. At points 2 and 3 carbonate deposition took place (thin facies A and B, respectively), but with frequent interruptions due to the lack of water caused by channel deviations for irrigation purposes.

Stretch 2, comprising tablets 4 to 12, had gravel and cobble deposits at sites 4 and 9, with very thin and sparse carbonate deposits. Downstream of these two sites, the sediment mainly consisted of algae- and moss-bearing tufa, stromatolite tufa and minor lime mud sediment. Within this stretch, points 10 and 11 were devoid of water for the most part of the summers between 2006 and 2009.

Stretch 3, comprising tablets 13 to 16, typically remained without or with very poor carbonate deposition. The highest values were measured at the furthest downstream point.

Deposition rates and environmental variations

Variations in depositional rates from almost -0.64mm/y to 4.53mm/y were recorded among the several subenvironments. Within every stretch, the lowest tufa deposition rates mostly corresponded to tablets in the river sites with more influence of groundwater inputs: sites 1, 4 and 13 (and most of stretch 3). In all cases, most of the sediment consisted of coarse detritals, facies C and thin and minor facies A, the latter generally with poor carbonate coatings. Successive mean yearly deposition values lower than 0 were caused by physical erosion of rolling clasts on the tablets.

Stretch 1 had the highest tufa deposition rates at site 3; despite the lack of water during some periods of the summer, mean yearly accumulation (3.63mm) was within the moderate-to-high deposition range ($3.5\text{--}4.5\text{mm/y}$; see Table I).

The highest tufa deposition rates were recorded in stretch 2 (Table I). Moderate-to-high mean yearly sedimentation rates (3.5 to 4.5mm/y) were recorded by tablets 6, 8, 10, 11 and 12. The highest rates corresponded

to tablet 6 (4.53mm/y), with moderate flow velocity (70 to 90cm/s), and to tablet 8 (4.21mm/y), with high flow velocity ($>100\text{cm/s}$). Both tablets 6 and 8 had similar water depth ($<15\text{cm}$). Tablet 12 recorded 4.29mm/y in slow flowing to dammed areas. Values around 2.5mm/y were obtained from tablets 5 and 7 placed in moderate to fast flowing conditions (74 to 105cm/s) and with depth between 15 and 25cm . The lowest rates in stretch 2 corresponded to tablets 4 and 9 (0.29 and 1.49mm/y), on gravel floors, with slow to moderate water flow and a mean depth from 15 to 20cm .

Stretch 3, with the greatest groundwater inputs from upstream sites, had moderate to high flow velocity and depth varied from 10 to 30cm . It showed very low to nil carbonate deposition rates (-0.64 to 1.09mm/y).

To sum up, although some relationships between tufa depositional rates and the several sedimentary subenvironments -mainly referred to water velocity and depth- can be inferred, these are not persistent since there are some exceptions. In some cases, the higher rates were obtained in fast flowing ($>90\text{cm/s}$) and shallow ($<15\text{cm}$) conditions. Lower rates were produced with increasing depth and decreasing water velocity.

As for relationships between deposition rates and the type of tufa facies, these do not seem to present a regular pattern of variation, and consequently similar water flow or depth conditions can produce either facies A, B or C (Table I). Exceptions are the slow flowing conditions in which only fine detrital sediment accumulated during floodings. Irrespective of water velocity and depth, the lowest tufa deposition rates corresponded to sites with more influence of groundwater; these coincided with an increase in conductivity, pCO_2 and other characters that was more noticeable in cool than in warm periods, and was particularly marked in the period of April 2006 to March 2008.

Variations of deposition rates over time

Deposition rates of the monitored sites decreased over time. The rates were higher from April 2003 to March 2006 than from April 2006 to September 2009. Mean yearly accumulation of all tablets was 3.02mm from 2003 to 2006, and 1.23mm from 2006 to 2009. Such a difference is more clearly marked by total accumulation in single tablets: of the 9 tablets that stayed in the river over the period of 2003–2009, 7 presented a much higher total accumulation

FIGURE 6 | Scanning electron microscope photomicrographs of tufa facies sampled from tablets at the time of measuring depositional rates. A, G: warm period of 2005; B, C, D, E, F, H) cool period of 2004–05. A–D: Facies A; A: Filamentous algae coated by calcite and diatoms. B: Detail of A, Calcite clumps on an alga filament, including diatoms. C: Moss leaf coated by calcite crystals and microbial components (cyanobacteria, diatoms, mucilage). D: Detail of C. E–G: Facies B; E: Laminae made of calcite tubes formed around cyanobacteria mostly arranged as adjacent bush-shaped bodies. F: Network of calcite tubes formed around cyanobacteria (Phormidium); smaller cyanobacterial filaments are present. G: Plan view of calcite tubes among micrite calcite, calcified mucilage and smaller microbial bodies in a hemidomic body. Notice the presence of a calcified filament of similar diameter than the interior of tubes (Phormidium). H: Facies C. Moss leaf with scarce sediment consisting of calcite clumps and diatoms.

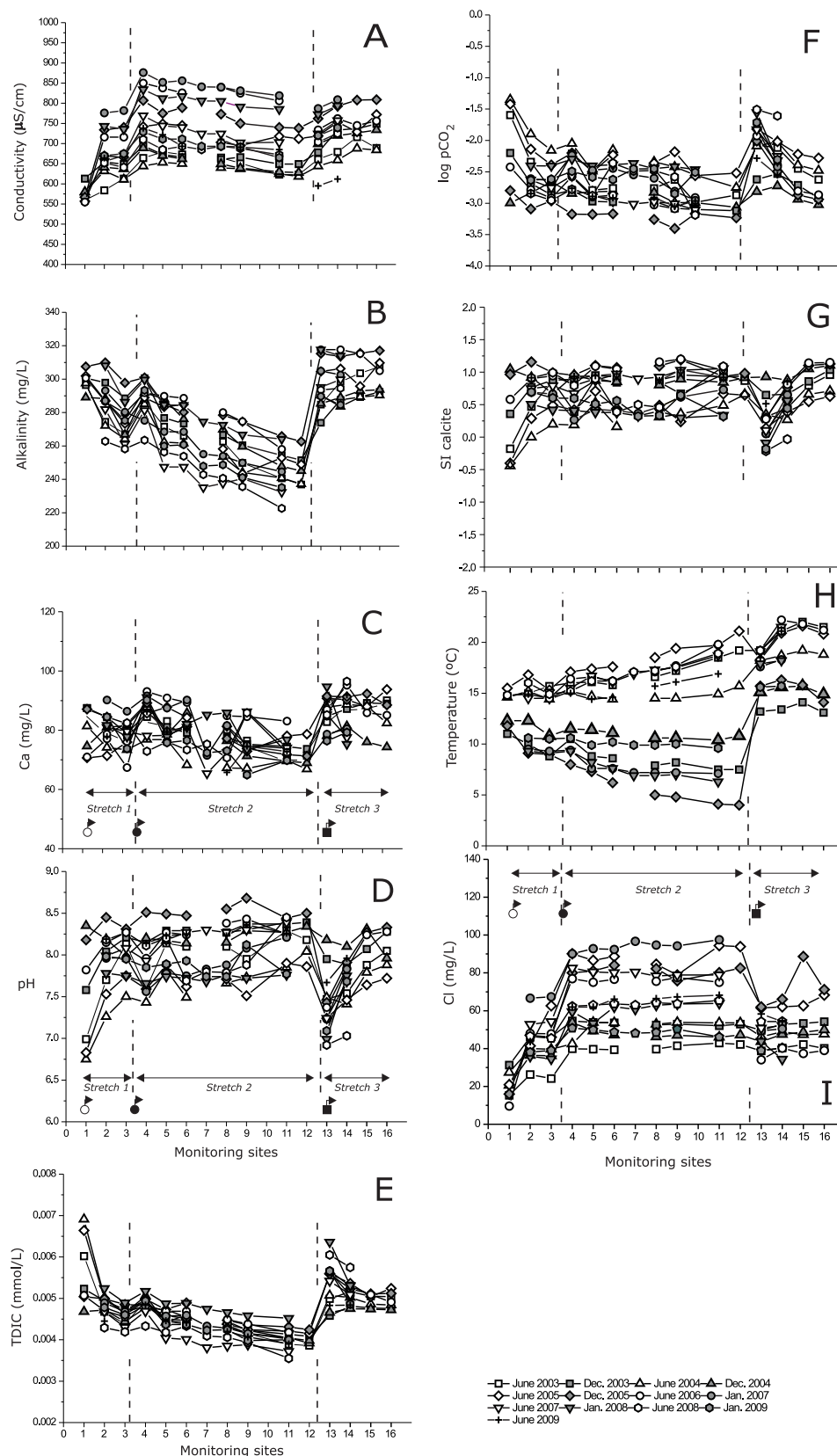


FIGURE 7 | Downstream hydro-chemical changes in A) conductivity, B) alkalinity (as HCO_3^-), C) calcium contents, D) pH, E) total dissolved inorganic carbon (TDIC), F) $\log p\text{CO}_2$, G) calcite saturation index (SI calcite), H) temperature and I) chloride contents along the River Mesa from June 2003 to June 2009. Open and filled symbols are used for warm and cold periods, respectively. Monitoring sites are indicated in Table I and Figure 2. Karstic and low-thermal discharges are indicated with the same symbols as in Figure 2.

during the period of April 2003–March 2006 than during the following 3.5 years. Similar conclusions are obtained if the periods considered are April 2003–September 2006 and October 2006–September 2009, despite the negative values due to strong erosion recorded in the warm period of 2006.

Considering the whole study period and all the tablets, the total mean six-monthly deposition rate was higher for the cool (1.88mm) than for the warm (0.16mm) periods (Table I). Mean six-monthly deposition rates of all tablets also showed the same pattern, with the only exception of the first two six-monthly periods (Fig. 8). The same trend was also displayed by six-monthly values of each tablet, with very few isolated cases out of this rule. The only significant exception was tablet 8, which mostly showed higher values in warm than in cool periods.

The aforementioned variation of yearly depositional rates over the monitored period was also detected by six-monthly deposition values. From April 2003 to March 2006, mean six-monthly deposition rates were 2.21mm in cool periods and 0.81mm in warm ones. From April 2006 to September 2009, these mean values diminished to 1.57 and -0.32mm, in cool and in warm periods, respectively.

The lowest six-monthly depositional rates were therefore recorded in warm periods (except April–September 2003; see single values of tablets in Table I), and were linked – at least partially or locally – to physical erosion. Erosional processes were recorded as negative values of thickness measurements. In addition, lower deposition values than the previous ones for cool periods, accompanied by visual features of erosion in the field and on the tablets (*e.g.*, scours and/or partial elimination of sediment deposited in previous periods), were also indicators of erosion. In some cases, the deposits of facies A found at the end of March were partially or totally absent at the end of September (see Fig. 5C, D). In contrast, those of facies B had higher preservation potential in the same conditions. Commonly, these cases with erosion coincided with heavy rain events primarily in May, July and August (Fig. 4).

DISCUSSION

The River Mesa shows a particular functioning pattern, quite different from standard patterns recorded in other tufaceous fluvial systems (*e.g.*, in Croatia, Emeis *et al.*, 1987; China, Liu *et al.*, 1995; Australia, Drysdale and Gillieson, 1997; Japan, Kawai *et al.*, 2006; Germany, Shiraishi *et al.*, 2008) and specially striking if compared to the nearby River Piedra. The Piedra and Mesa rivers share the same water divide, climatic conditions and source aquifer (Sierra del Solorio aquifer, Servicio Geológico de Obras Públicas, 1990). Furthermore, both show similar hydrochemical

TABLE 1 | Hydrochemical characters of some representative thermal springs around Jaraba. Concentrations in mg/l. Saturation index and log pCO₂ values are calculated with PHREEQC (Parkhurst and Appelo, 1999) and the WATQEF thermodynamic database (Ball and Nordstrom, 2001). San Luis and Las Pilas data are from Auqué *et al.* (2009). Huerta de la Hoz thermal spring data, near point 13 (see Fig. 2 for location of springs)

	San Luis	Las Pilas	Huerta de la Hoz
Temperature (°C)	32.0	26.6	20.9
Conductivity (µS/cm)	910	865	632
pH	7.04	7.40	7.30
Alkalinity (as HCO ₃ ⁻ , mg/L)	281.9	288.6	316.6
Cl ⁻ (mg/L)	59.2	50.0	45.4
SO ₄ ²⁻ (mg/L)	147.9	126.8	117.6
Ca ²⁺ (mg/L)	96.6	92.6	96.5
Mg ²⁺ (mg/L)	40.8	42.3	31.2
Na ⁺ (mg/L)	34.5	32.2	26.9
K ⁺ (mg/L)	1.2	1.2	3.1
SI calcite	+0.02	+0.30	+0.19
log pCO ₂	-1.57	-1.96	-1.85

characters and their discharges evolved with a similar pattern during the monitored period. The most conspicuous differences between the rivers Mesa and Piedra are:

i) Tufa sedimentation in the River Mesa mostly occurs in association with filamentous algae, mosses and cyanobacterial mats. Algae and mosses generally had poor to moderate carbonate coatings and impregnations, and laminated carbonate deposits were thin and not extensive. Our study indicates that there was not a persistent pattern that related water flow velocity and depth to deposition rates through the studied period. Neither was there a consistent relationship between these parameters and the type of sedimentary facies. In contrast, the River Piedra shows a clear relationship between flow parameters, types of tufa facies and depositional rates (Vázquez-Urbez *et al.*, 2010 and 2011). Other tufa-depositing rivers also present such relationships (*e.g.*, Liu *et al.*, 1995, Drysdale and Gillieson, 1997; Merz-Preiß and Riding, 1999).

ii) In the River Mesa, the measured deposition rates show higher values in cool than in warm periods, with the only exception of the first monitored year (Fig. 8). As for subenvironments, most sites with significant tufa sedimentation presented this pattern, except tablet 8 (Table I). In the River Piedra the higher depositional rates were measured in warm periods, from 1999 to 2010 (Arenas *et al.*, 2010; Vázquez-Urbez *et al.*, 2010, 2011), which suggested that temperature was the main factor inducing this depositional pattern.

iii) Groundwater inputs along the River Mesa course, coupled with the gentle gradient profile, are the most important distinctive features with respect to the River Piedra. Groundwater inputs in the River Piedra

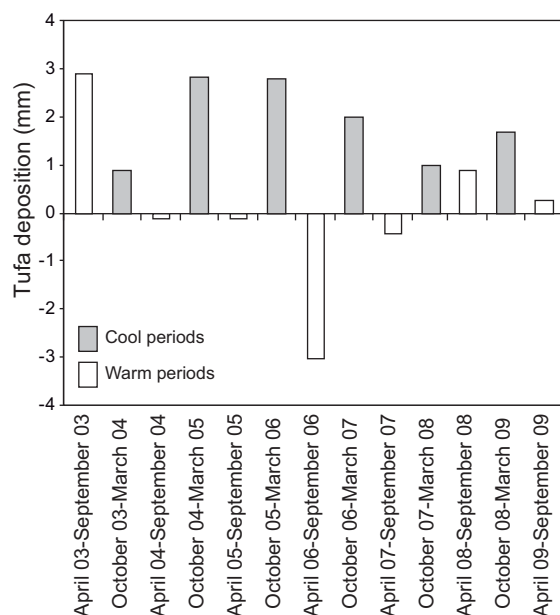


FIGURE 8 | Mean six-monthly tufa deposition recorded by all tablets through the study period. Cool periods (autumn+winter) show higher values than warm ones (spring+summer), with the exception of the first two monitored six-monthly periods. The negative values recorded during some warm periods are associated, at least partially, with erosional processes, in particular those caused by strong storms in the warm period 2006.

are only detected at headwaters and at the lower reach, downstream of the Monasterio de Piedra Natural Park. Therefore, the spatial pattern of variation of that river is controlled by continuous water CO_2 -loss through space enhanced by several significant topographic breaks along its profile (*e.g.*, waterfalls). In contrast, the River Mesa has a general low gradient profile with gentle topographic changes that do not induce rapid or great water CO_2 -loss.

In brief, in the River Mesa it is not possible to establish a causal relationship between tufa sedimentation characteristics and some processes that are commonly argued to explain variations in fluvial tufa sedimentation rates: continuous CO_2 degassing through mechanical processes and photosynthesis, and changes in temperature that affect calcite solubility, precipitation rate and that favour plant development in warm periods (Drysedale and Gillieson, 1997; Merz-Preiß and Riding, 1999; Lu *et al.*, 2000; Chen *et al.*, 2004; Shiraishi *et al.*, 2008; Vázquez-Urbez *et al.*, 2010). Likely, the influence of other factors in the River Mesa made the abovementioned ones indistinct.

Spatial variations in the River Mesa system

The lowest tufa deposition rates in the River Mesa corresponded to the river parts that received most

groundwater inputs (points 1, 4 and 13), which implied a sharp increase in pCO_2 and conductivity of the river water close to the outflow points. Downstream of these inputs, tufa sedimentation increased in the first and, especially, in the second stretch, although it was almost nil along the third stretch.

The first stretch had an irregular hydrochemical behaviour, probably induced by runoff from point 1. This situation would prevent or delay the usually “normal” evolution towards carbonate precipitation (by CO_2 outgassing); as a result, significant carbonate deposition only took place at the most downstream sites monitored in this stretch (some 3km away).

In the second stretch, with groundwater input at point 4, the downstream evolution of the hydrochemical characters indicates effective tufa deposition. Moreover, total tufa sedimentation recorded in tablets increased downstream and, although this trend was not progressive, it would be consistent with the increasing loss of dissolved CO_2 . This is a common process in tufa-depositing streams (Drysedale *et al.*, 2002).

Finally, the large and almost constant volume of low-thermal water discharge along the third stretch “resets” and conditions the hydrochemical characters of the River Mesa water. The hydrochemical evolution of some parameters does not support the presence of significant tufa precipitation (*e.g.*, almost constant contents of alkalinity, Ca^{2+} , TDIC), although the SIc increased downstream and some minor precipitation may occur at the end of the stretch. Accordingly, tablets installed in this stretch did not record considerable carbonate sedimentation (except tablet 16, at the more downstream point; Table I) and showed minimal variations through space, which accords with the presence of several spring inputs through its course.

Overall, the points at which tufa sedimentation occurred were located well downstream of the identified groundwater discharges in the River Mesa. Important groundwater inputs (*e.g.*, Jaraba springs) promoted a “ CO_2 recharge” in the river waters (decreasing SIc and increasing pCO_2 values). Thus, from the sites of groundwater inputs, a certain distance (*e.g.*, kilometres, as it occurs in other tufa-depositing rivers; Drysedale *et al.*, 2002; Fig. 2) is needed to reach the necessary SIc values (through CO_2 outgassing) to overcome the kinetic barrier to precipitation and resume tufa sedimentation.

However, none of the aforementioned mechanisms explain the seasonal and pluriannual trends observed in the River Mesa.

Temporal variations in the River Mesa system

The three stretches differentiated in the River Mesa also show distinct temporal evolutions. In the first stretch, the CO_2 partial pressures at point 1 are higher in summer

than in winter and, accordingly, pH values are lower in summer. Moreover, as the SIc values correlate negatively with $p\text{CO}_2$, a seasonal pattern for SIc values is also clear at point 1, SIc being higher in the cool period and lower in the warm period. This seasonal behaviour may be due to two processes: i) gas exchange with the raised warm-period $p\text{CO}_2$ in the soil; and ii) ventilation of limestone caves air in winter, favoured by the higher difference in density between the air in the aquifer and the atmosphere (*e.g.* Kano *et al.*, 2003; Kawai *et al.*, 2006; Hori *et al.*, 2008). However, downstream of point 1 the hydrochemical characters are affected by runoff influx that induces, for example, increases in the conductivity irrespective of the monitoring period. Tufa deposition at points 2 and 3 showed frequent interruptions due to the lack of water in the warm periods of the 2006–2008 interval; channel deviations for irrigation purposes helped such deposition interruptions. As a consequence, depositional rates in these sites cannot be taken as representative of natural conditions.

Along the third stretch, the large and constant low-thermal water discharge minimizes the effects of any temporal changes in runoff supply in the river and impedes the development of any temporal (*e.g.*, seasonal) hydrochemical trend. The observed changes in the hydrochemical characters through the studied period in this stretch are mainly related to variations in the mixing proportions between the surficial and the low-thermal waters. Mixing processes between thermal and cool river waters can be sufficient to impede significant carbonate precipitation (Herman and Lorah, 1988).

Focussing the discussion on the second and longest stretch (Fig. 2), tufa sedimentation shows the reverse seasonal behaviour to that observed in the River Piedra (see above). Moreover, two different intervals can be differentiated: from April 2003 to March 2006 and from April 2006 to September 2009 (Table I); these are separated by the maximum decrease in water discharge in the warm period of 2006 (Fig. 4). These two intervals show distinct tufa deposition rates and chemical characters of the river water (Figs. 7; 8). The total amount of sediment accumulated in the tablets (neglecting those with negative values) was higher (both in the cool and warm periods) in the first interval than in the second one. Some hydrochemical characters (*e.g.*, conductivity values, Na^+ and Cl^- concentrations; see above) partially agree with these two intervals. However, other compositional characters (alkalinity, TDIC, Ca^{2+} and SIc) do not clearly parallel this temporal trend, although the highest values were reached during the drought period (second interval). This situation probably reflects the low sedimentation rate recorded in this period, but this issue needs further study.

Mean water discharge displayed temporal variations parallel to those of sedimentation rates (Table I; Fig. 9).

Discharge decreased through time in both warm and cool periods, from extreme values of 2.77–1.31 m³/s in the interval of April 2003–March 2006, to lower values of 1.57–0.76 m³/s in the interval of April 2006–September 2009 (Fig. 4). Therefore, the overall decrease in yearly deposition rates from 2006 to 2009 can be attributed, at least partially, to the parallel reduction in mean discharge (Fig. 9), which partially correlates with a decrease in rainfall from March 2005 to March 2008 (Fig. 4). The discharge decrease coincides with increasing Cl^- , Na^+ and conductivity values from June 2005 to January 2008 (Table II). The influence of water discharge in the calcite precipitation rate (higher with higher discharges) has been highlighted and discussed in other tufa-precipitating streams (*e.g.*, Kawai *et al.*, 2006). In addition, in the River Mesa a greater river water derivation for agriculture uses upstream of Jaraba springs helped the drying out process of some sites in the second stretch (*i.e.*, between Calmarza and Jaraba villages) in the summer. Qualitative information supplied by local village councils indicates that water demand during the summer surpasses the river water resources. Thus the tablets were subaerially exposed, resulting in tufa deposition cessation during that time. These sites were more liable to erosion when water flowed again due to their loose state by previous dessication.

The decrease in discharge in warm periods, particularly in the driest ones, implied that most, or at least a great portion, of the river water corresponded to groundwater that entered the river at points 1, 4 and all of stretch 3. Indeed, runoff –although limited to summer storms– would be enriched in CO_2 from soils. Thus, these inputs of higher $p\text{CO}_2$ (and, therefore, lower pH) waters to the river water could have caused a decrease in calcite precipitation in some warm periods.

Erosion processes (*e.g.*, scours on the tablets and/or partial elimination of sediment deposited in previous periods) have been detected in almost all of the warm periods during the monitoring study. High discharge occurring in short moments of spring and summer (*e.g.*, caused by high rainfall in May and June 2004, 2006 and 2007) could cause erosion and explain the negative and low deposition rates in those warm periods. In addition, the tablets in sites that were subjected to temporary drying in the warm periods recorded very low sedimentation rates, commonly with negative values. In the warm periods of the drought stage (2006–2008), these erosional processes were more generalized and/or intense, lowering even further the thickness of sediment deposited on the tablets.

Briefly, the main causes that controlled sedimentation features appear to be related to: i) The influence of groundwater in equilibrium or at very low saturation with respect to calcite, ii) Soil-derived CO_2 inputs along the

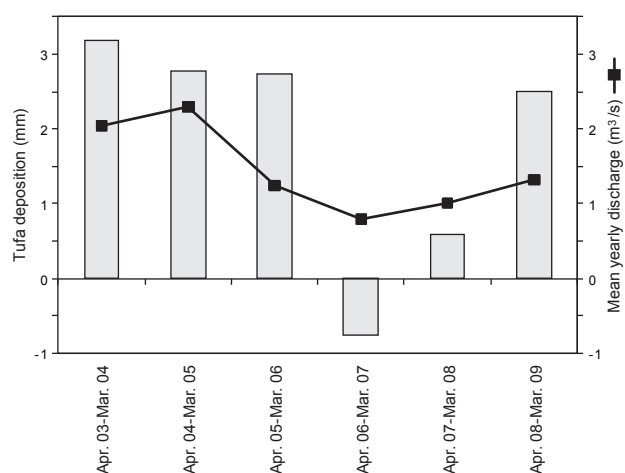


FIGURE 9 | Variations of yearly depositional rates (see Table I) and discharge of the River Mesa from 2003 to 2009.

river course, iii) Erosional events related to heavy rain or storms, and iv) Episodes of changes in river discharge related to variations in amount of rainfall through time. The effects of other environmental factors such as water velocity, depth and air temperature on sedimentation rates and types of facies probably became blurred by the factors mentioned above.

CONCLUSIONS

In the lower 27km-long stretch of the River Mesa, 16 sites, representing different sedimentary subenvironments, were selected for periodical monitoring over 6.5 years (April 2003 to September 2009). Tufa deposition rates, hydrochemical and hydrophysical features were studied every six months. From this study several conclusions can be drawn.

The mean annual sedimentation rate was of about 2mm/y. Sites with the highest deposition rates consisted of sediment made of: i) filamentous algae associated with cyanobacterial and moss mats and diatoms constituting a porous tufa fabric, and ii) laminated carbonate deposits (stromatolites) and calcified microbial mats, which made up a dense fabric. They formed in small, generally stepped jumps, rapids and subhorizontal floors with flow velocity between 70 and 120cm/s.

Mean six-monthly sedimentation rates were higher in cool (1.88mm) than in warm (0.16mm) periods; this trend is the opposite to the one commonly observed in many fluvial tufa systems. The influence of water-CO₂ degassing and temperature-dependent processes (*e.g.*, calcite solubility and flora development) were probably overprinted by other

factors: the occurrence of drought stages and water use for irrigation during summer minimized the water flow. In such conditions, higher pCO₂ in the river water -mostly from groundwater- was expected to limit calcite precipitation. In addition, carbonate deposition was inhibited in the parts of the channel floor which were subaerially exposed. Moreover, strong flooding events during the warm periods promoted erosion. The remarkable decrease in tufa deposition rates from 2006 to 2009 is consistent with an important reduction in river discharge, which partially correlates with a decrease in rainfall.

The systematic study of hydrochemical characters along the River Mesa has enabled detection of karstic inputs that were unknown to the present (*e.g.*, around site 4).

The occurrence of several groundwater discharge points, with variable thermochemical nature along the river, is a main factor controlling the sedimentation characteristics along the River Mesa system. Three stretches were identified in the studied Mesa River course based on these subsurface water inputs (karstic springs and low-thermal discharges).

The lowest tufa deposition rates correspond to sites with more influence of groundwater inputs. The highest tufa deposition rates (mean of 4mm/y) were recorded in the intermediate stretch, in fast flowing conditions (>90cm/s). General decreasing trends in conductivity, alkalinity, TDIC values and calcium concentrations and permanent positive values of SI_c were observed along this stretch.

This work evidences that fluvial tufa dynamics in Mediterranean climate environments is highly influenced by spatial (distribution of steady groundwater discharges), seasonal (droughts, water use for irrigation and floods during spring-summer periods) and yearly (mean river discharge related to rainfall) changes in hydrological conditions.

Results on factors controlling sedimentation rates and hydrochemical variations are more accurate when the monitoring studies span time periods of several years. Short-time studies (*e.g.*, of 1 or 2 years) may lead to biased conclusions as some factors controlling sedimentation may be underestimated or not even considered. In the case of the River Mesa, conclusions would have been dramatically different if only the first year of monitoring had been considered (Table I).

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ELECTRONIC APPENDIX

TABLE I Sedimentation rates from tablets and their sedimentary environmental conditions and facies monitored from 2003 to 2009													
Sedimentary environmental conditions				Deposit on tablets	Six-monthly accumulation (mm)								
Tablet nº	Sedimentary features of the bed	Depth (cm) Warm Cool	Flow velocity (cm/s) Warm Cool	A, B, C, D: tufa facies	April 03- September 03	October 03- March 04	April 04- September 04	October 04- March 05	April 05- September 05	October 05- March 06	April 06- September 06	October 06- March 07	April 07- September 07
1	Gravel bed on subhorizontal floor	12.60 13.75	86.72 93.62	Gravel deposits Sparse C	0.00	0.19	-0.16	0.19	-0.18	0.09	-0.26		
2	Small jumps or rapids	11.76 11.67	84.98 66.92	A, (B)	0.32	1.00	0.69	2.01	1.44	-5.60	0.92	1.32	0.14
3	Small jumps or rapids	10.77 10.67	107.82 118.38	B, (A)	6.56	1.55	-5.90	5.09	3.19	1.18	7.50	0.78	0.56
4	Irregular gravel bed, with cobbles	15.84 16.29	79.70 84.27	C	0.13	-0.24	-0.26	0.58	0.82	-0.33	0.83	0.82	-1.24
5	Small stepped jumps	23.16 24.63	105.71 105.73	A	2.61	0.56	-2.32	1.24	1.13	28.68	-25.01	4.54	-2.58
6	Subhorizontal platform	14.70 14.42	74.02 80.31	B, A	3.91	4.96	2.54	5.10	2.05	8.52	-9.31	1.81	-0.27
7	Small jumps and rapids	18.71 17.83	75.43 91.34	A, (B)								7.91	-3.60
8	Small stepped jumps	12.41 13.54	109.65 102.55	A	7.61	1.82	2.94	1.25	-0.73	1.26	--	1.75	2.41
9	Irregular gravel bed, with cobbles	13.59 20.38	41.44 54.72	A	7.51	-4.09	0.03	2.94	-1.10	3.80	-3.53	0.70	0.79
10	Irregular horizontal bed with cobbles	15.40 24.50	65.28 78.50	B	3.76	3.24	0.37	2.28	1.10	1.05	--		
11	Small stepped jumps	9.20 13.63	109.31 94.24	A, (B)	4.02	3.27	2.06	6.32	-4.65	0.61	--	-0.06	0.15
12	Subhorizontal bed with cobbles upstream of stepped jumps	25.0 45.25	27.67 35.44	D, (A)	1.37	0.47	-0.59	13.99	-3.81	0.23	0.62		
13	Gravel bed on subhorizontal floor	21.45 21.70	66.25 75.06	Gravel deposits Sparse C	--	-0.09	--	-0.20	-0.49	-0.18	--		
14	Subhorizontal platform (gauging point)	10.49 12.88	116.16 97.89	C	--	0.33	--	0.54	--	1.34	-1.86	0.39	-0.44
15	Irregular gravel bed, with cobbles	27.20 30.50	100.00 111.37	Coarse detritals C	-0.13	-0.01	-0.37	0.31	-0.27	0.58	0.15		
16	Irregular gravel bed, with cobbles	15.80 20.00	83.31 89.50	Coarse detritals C, (A)	0.25	--	-0.34	1.28	0.13	1.12	--		
Total accumulation of each period					37.93	12.94	-1.32	42.93	-1.37	42.33	-29.95	20.06	-4.08
Mean of each case (columns)					2.92	0.92	-0.10	2.86	-0.10	2.82	-3.00	2.01	-0.41

TABLE I | Continued

Tablet n°	Six-monthly accumulation (mm)				Apr 2003-Mar 2006				Apr 2006-Sept 2009				Apr 2003-Sept 2009				Total accumulation (mm)			Mean yearly accumulation (mm) 2003-2009
	October 07- March 08	April 08- September 08	October 08- March 09	April 09- September 09	Mean of cool periods	Mean of warm periods	Mean of cool periods	Mean of warm periods	Mean of cool periods	Mean of warm periods	Mean of cool periods	Mean of warm periods	Mean of cool periods	Mean of warm periods	April 03- March 06	April 06- September 09	April 03- September 09			
1					0.16	-0.11		-0.15	0.16	-0.15		-0.15	0.16	-0.15	-0.13		-0.13	0.01		
2	0.91	1.68	0.43	--	-0.86	0.81		0.91	0.01	0.86		0.86	0.01	0.86	-0.15	5.40	5.25	0.87		
3	1.24	-1.70	1.73	--	2.61	1.29	1.25	2.12	1.93	1.70		1.70	1.93	1.70	11.67	10.11	21.78	3.63		
4	-0.03	-0.32	0.53	0.33	0.01	0.23	0.47	-0.10	0.24	0.05		0.05	0.24	0.05	0.70	1.03	1.73	0.29		
5	3.08	0.37	3.67	-0.39	10.16	0.47	3.76	-6.90	6.96	-4.37		-4.37	6.96	-4.37	31.89	-16.33	15.57	2.59		
6	3.24	--	0.60	4.06	6.19	2.83	1.88	-1.84	4.04	0.50		0.50	4.04	0.50	27.08	0.12	27.20	4.53		
7	1.05	2.01	-0.41	0.41			2.85	-0.39	2.85	-0.39		-0.39	2.85	-0.39		7.38	7.38	2.46		
8	-0.44	3.80	2.31	1.28	1.44	3.27	1.21	2.50	1.32	2.89		2.89	1.32	2.89	14.15	11.11	25.26	4.21		
9	0.53	0.16	9.37	-8.85	0.88	2.15	3.53	-2.86	2.21	-0.71		-0.71	2.21	-0.71	9.08	-0.84	8.24	1.49		
10					2.19	1.75			2.19	1.75		1.75	2.19	1.75	11.81		11.81	3.94		
11	0.07	0.69	0.66	5.94	3.40	0.47	0.22	2.26	1.81	2.02		2.02	1.81	2.02	11.63	7.44	19.08	3.83		
12					4.90	-1.01		0.62	4.90	-0.60		-0.60	4.90	-0.60	11.66	0.62	12.28	4.29		
13					-0.16	-0.49			-0.16	-0.49		-0.49	-0.16	-0.49	-0.96		-0.96	-0.64		
14	0.39	1.46	-1.98	-0.46	0.74		-0.40	-0.33	0.17	-0.33		-0.33	0.17	-0.33	2.21	-2.50	-0.29	-0.16		
15					0.29	-0.26		0.15	0.29	-0.16		-0.16	0.29	-0.16	0.10		0.25	0.13		
16					1.20	0.01			1.20	0.01		0.01	1.20	0.01	2.44		2.44	1.21		
	10.04	8.15	16.90	2.32	33.13	11.39	15.66	-4.12	30.15	2.62		2.62	30.15	2.62	133.18	23.54	156.87	32.77		
	1.00	0.91	1.69	0.29	2.21	0.81	1.57	-0.32	1.88	0.16		0.16	1.88	0.16				2.05		

TABLE II | Hydrochemical data for the different sampling periods (from June 2003 to June 2009) in the River Mesa

	Temperature (°C)	Conductivity (µS/cm)	pH	Alkalinity (as HCO ₃ , mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)
June 2003										
1	14.7	559.0	6.99	296.46	15.30	61.90	10.55	3.55	85.98	20.67
2	15.0	584.0	7.70	274.50	26.30	51.90	20.89	2.89	79.73	20.99
3	15.7	613.0	8.13	267.18	24.15	67.80	20.65	1.64	76.68	21.14
4	16.0	664.0	7.59	286.22	39.90	84.70	28.00	2.10	83.00	24.00
5	16.1	679.0	8.14	271.58	39.65	81.60	31.08	1.96	81.59	22.29
6	15.8	673.0	8.10	265.96	39.39	78.90	30.58	1.87	79.61	21.73
8	16.6	665.0	8.10	262.54	39.65	77.80	31.27	1.95	78.62	22.28
9	17.2	651.0	7.95	249.86	41.50	77.80	31.03	1.96	74.98	22.11
11	18.5	623.0	8.29	240.58	42.90	77.30	30.74	2.08	69.99	21.82
12	19.2	623.0	8.18	236.92	42.20	74.70	31.05	1.94	69.91	21.99
13	19.2	661.0	7.47	284.74	38.80	73.60	27.93	2.08	81.27	23.88
14	21.1	679.0	7.54	298.42	40.35	87.90	29.45	2.16	86.79	27.61
15	22.0	716.0	7.88	303.54	42.20	89.00	29.60	2.20	87.00	28.10
16	21.5	689.0	8.05	307.44	40.10	98.50	29.72	2.26	88.58	29.55
December 2003										
1	11.00	613.00	7.58	300.55	31.30	55.48	13.42	5.19	86.00	20.15
2	10.00	654.00	8.04	297.90	46.00	62.34	21.61	4.59	82.90	20.07
3	8.80	649.00	8.21	288.53	46.20	61.20	20.98	3.45	77.40	19.67
4	10.50	694.00	8.15	300.55	54.60	65.20	26.66	2.35	84.50	20.33
5	8.80	673.00	8.29	276.75	53.80	63.48	27.14	2.33	79.60	20.47
6	8.60	666.00	8.29	273.38	53.60	64.06	26.93	2.12	77.60	21.07
8	7.90	661.00	8.27	266.65	52.50	72.63	26.92	2.19	76.10	21.15
9	8.20	666.00	8.37	260.40	52.90	65.77	27.03	2.04	73.80	21.21
11	7.50	649.00	8.37	254.39	52.10	64.06	26.93	1.92	73.00	21.14
12	7.50	649.00	8.39	251.50	52.90	72.06	26.82	1.95	72.20	21.57
13	13.20	678.00	7.95	273.86	49.60	68.06	25.65	1.91	83.20	23.01
14	13.40	734.00	7.89	287.57	52.90	76.63	26.93	1.98	85.70	25.95
15	14.10	737.00	8.07	289.25	53.30	82.92	26.55	1.98	87.70	26.81
16	13.10	749.00	8.28	292.38	54.20	83.49	26.66	2.07	87.50	27.66

TABLE II | Continued

June 2004										
1	14.6	579.0	6.75	297.46	27.4	54.85	13.06	3.03	79.9	20.23
2	15.2	632.0	7.26	272.12	40.0	58.13	20.47	2.70	72.7	20.00
3	14.4	611.0	7.50	264.23	39.7	60.81	20.63	2.17	71.9	20.33
4	15.2	644.0	7.43	285.03	42.5	64.26	27.02	1.97	75.4	21.11
5	14.7	653.0	7.82	262.31	53.8	69.75	27.26	1.92	75.3	20.79
6	14.4	650.0	7.49	261.60	53.7	64.17	27.25	1.87	66.8	20.80
8	14.5	640.0	7.66	253.47	52.9	62.43	27.11	1.84	65.8	20.97
9	14.5	637.0	7.73	244.14	53.8	63.49	27.14	1.87	65.6	21.09
11	14.9	625.0	7.85	240.79	53.6	65.58	26.87	1.89	68.3	21.09
12	15.7	618.0	8.04	237.21	53.6	66.77	26.95	1.94	65.4	20.84
13	18.2	644.0	7.49	290.29	46.3	64.09	23.78	2.02	86.3	25.22
14	18.7	659.0	7.41	283.60	48.8	72.73	25.27	2.04	87.2	25.33
15	19.2	688.0	7.79	289.33	47.4	78.98	25.43	2.02	86.7	25.99
16	18.8	684.0	7.88	290.29	47.6	81.96	25.50	2.12	80.9	26.04
December 2004										
1	12.3	580	8.35	289.05	20.6	53.16	18.09	2.51	73.10	19.70
2	12.3	641	8.19	288.36	36.4	62.84	19.98	2.45	79.50	20.20
3	10.8	637	7.98	266.80	36.2	62.28	19.72	2.64	80.10	20.24
4	11.5	689	8.2	291.84	53.8	64.81	26.34	1.97	87.10	20.86
5	11.4	670	8.17	288.13	49.3	63.41	26.21	2.07	77.10	20.75
6	11.1	662	8.14	276.07	47.2	79.36	26.14	2.11	84.30	20.76
8	10.6	649	8.15	269.82	46.2	64.55	25.99	2.03	74.90	20.79
9	10.6	639	8.29	259.62	47	65.81	25.51	2.07	69.80	20.78
11	10.4	630	8.27	247.79	46	61.71	25.61	2.02	68.10	21.00
12	10.8	628	8.34	245.01	47.2	45.19	25.38	2.00	67.50	20.76
13	15.1	699	8.18	285.35	43.7	57.72	23.16	2.08	76.60	24.64
14	15.6	720	8.1	289.05	47.5	63.41	24.50	2.17	79.90	25.79
15	15.7	726	8.31	293.00	48.7	68.54	25.00	2.18	74.50	26.42
16	14.9	734	8.39	293.69	49.9	67.66	25.39	2.29	72.80	27.26

TABLE II | Continued

June 2005										
1	15.5	557	6.83	301.91	20.9	40.05	7.97	2.75	69.2	22.23
2	16.8	669	7.53	287.02	41.4	52.48	28.52	2.36	69.9	20.43
3	15.3	666	7.75	273.35	62.6	60.87	28.98	2.49	74.5	20.49
4	17.1	742	7.59	288.97	90.1	68.56	44.06	2.90	84.2	21.95
5	17.4	749	7.88	283.36	86.6	66.91	42.19	3.18	86.3	22.44
6	17.6	745	7.62	284.82	88.7	65.82	42.25	3.19	82.8	22.21
8	18.5	703	7.71	258.22	84.6	60.87	38.72	3.68	79.8	21.37
9	19.4	695	7.51	243.33	78.9	61.97	36.52	6.01	71.4	18.88
11	19.7	718	7.9	252.85	94.4	66.91	43.02	3.37	76.6	21.88
12	21.1	712	7.86	248.94	93.9	60.32	43.26	3.52	77.2	21.56
13	18.3	719	7.24	304.59	61.4	50.44	24.99	2.78	89.3	26.27
14	20.9	753	7.46	306.30	62.1	64.17	29.23	3.14	88.8	29.04
15	21.6	729	7.64	295.81	62.6	67.46	26.97	4.10	86.5	28.66
16	20.8	772	7.72	309.72	68.3	74.05	29.37	3.19	92.3	31.64
December 2005										
1	11.8	567	8.18	307.52	16.00	53.50	7.44	3.08	85.60	20.27
2	9.1	734	8.45	309.96	47.00	65.23	33.01	2.47	83.00	21.02
3	9	740	8.31	297.76	46.00	70.78	32.59	2.05	80.70	20.90
4	8	807	8.51	300.93	80.00	78.38	45.52	2.49	87.70	21.93
5	7.3	775	8.49	284.82	81.00	73.05	45.11	2.37	78.10	22.39
6	6.2	789	8.47	280.19	84.02	72.36	45.28	2.58	79.70	22.35
8	5	773	8.55	278.48	82.20	80.84	45.56	2.39	75.70	22.27
9	4.8	750	8.68	274.57	75.90	80.17	46.39	2.40	72.30	21.90
11	4.1	740	8.44	265.79	80.10	79.26	45.72	2.42	70.30	21.98
12	4	738	9	262.61	82.50	78.82	45.89	2.35	69.80	22.00
13	15.7	762	7.43	315.33	62.00	86.92	28.10	2.15	90.00	27.75
14	16.3	793	7.91	313.62	66.10	90.98	31.27	2.37	89.80	29.18
15	15.8	808	8.27	315.57	88.70	95.88	30.08	2.66	90.80	31.22
16	14.1	809	8.33	317.04	71.15	91.20	31.50	2.44	87.00	31.16

TABLE II | Continued

June 2006										
1	14.8	555	7.82	300.66	9.6	30.48	6.84	2.19	69.5	20.07
2	14.9	716	8.15	286.54	48.0	38.87	38.41	2.23	75.6	20.94
3	14.5	716	8.27	279.61	47.8	39.19	35.63	2.25	65.9	20.83
4	16.4	850	7.96	291.81	76.9	63.39	44.68	2.96	91.6	23.22
5	16.6	838	8.27	289.89	75.0	62.74	50.69	2.87	89.4	23.21
6	16.2	826	8.24	288.70	76.6	62.74	52.13	2.80	87.9	23.40
8	17.1	840	8.38	280.09	75.6	63.71	55.26	2.97	83.4	23.45
9	17.7	825	8.43	274.59	77.5	65.97	54.54	3.05	83.1	23.43
11	19.8	806	8.25	258.08	75.0	69.84	54.36	3.22	81.6	23.64
13	19.2	734	7.37	317.64	34.1	62.42	24.88	2.27	85.5	28.73
14	22.2	762	7.84	317.64	40.2	70.97	27.04	2.43	93.7	31.14
15	21.8	745	8.24	315.25	37.4	70.48	27.15	2.36	84.4	31.56
16	21.2	756	8.28	304.96	39.0	80.81	27.75	2.73	83.6	32.34
January 2007										
2	9.5	776	7.96	293.1	66.6	81.5	44.7	5.04	88.7	21.44
3	9.3	782	7.97	280.3	67.4	78.1	44.9	4.37	84.9	21.59
4	9.4	876	7.56	275.2	90.1	91.3	61.3	4.08	90.1	23.67
5	7.6	852	7.78	268.5	92.8	91.8	60.1	3.14	86.0	23.49
6	7.6	856	7.75	268.5	92.4	102.0	60.2	3.62	88.7	23.78
7	7.2	841	7.83	255.1	96.7	95.2	62.0	6.31	70.0	23.54
8	7.2	840	7.88	253.9	94.7	94.2	61.8	3.15	80.1	23.65
9	7.2	831	8.08	249.9	94.3	103.5	60.2	4.58	73.4	23.30
11	7.1	819	8.21	244.6	97.5	93.2	61.0	4.95	72.4	23.74
13	17.6	787	7.23	304.9	49.4	74.2	29.0	4.36	77.2	28.80
14	18.3	809	7.83	302.6	50.4	96.6	33.0	3.10	79.0	31.23
June 2007										
2	14.5	656	7.99	281.95	52.80	63.95	29.62	2.29	79.50	20.63
3	14.5	670	8.08	261.08	54.20	72.87	29.19	2.26	78.10	20.75
4	15.5	769	7.93	281.25	82.50	80.75	50.89	2.69	76.60	22.71
5	16.7	744	8.18	247.40	80.50	90.20	54.72	2.63	76.80	22.63
6	16.1	740	8.27	247.40	80.10	83.37	48.25	2.34	79.60	22.59
7	16.9	724	8.30	235.11	80.40	83.90	53.93	2.64	63.90	22.49
8	17.3	724	8.27	237.66	78.40	79.17	53.70	2.45	71.00	22.82
9	17.5	702	8.30	240.44	78.90	80.22	52.12	2.34	84.80	22.32
11	18.7	703	8.39	232.33	78.90	79.70	40.95	2.73	72.60	22.57
13	19.1	724	7.24	295.16	50.80	82.32	26.81	2.26	83.80	27.14
14	21.5	757	7.68	299.80	52.20	85.12	28.99	2.60	76.10	29.56

TABLE II | Continued

January 2008										
2	9.3	743	7.78	308.13	35.90	58.31	36.30	1.34	80.20	21.80
3	9.1	736	7.75	286.32	34.50	71.19	36.80	1.91	76.30	22.16
4	9.3	834	7.66	299.65	59.50	73.90	52.10	2.62	89.60	23.59
5	8.2	812	7.74	284.63	53.30	82.03	53.90	4.08	76.30	23.07
6	7.6	817	7.72	284.39	62.00	73.56	54.10	3.88	80.60	23.50
7	6.9	806	7.68	274.45	60.80	73.56	52.90	3.71	83.70	23.57
8	6.9	805	7.76	272.52	62.90	87.12	52.80	3.19	84.40	23.43
9	7.0	791	7.72	266.70	63.50	75.25	53.50	2.98	72.10	23.21
11	6.3	785	7.76	264.04	63.90	78.64	52.30	3.10	75.30	23.47
13	17.9	772	6.99	317.57	43.80	75.25	29.10	2.78	93.20	31.00
14	18.2	794	7.75	313.94	34.40	93.90	31.60	3.76	73.80	29.64
June 2008										
2	16.0	652	8.18	262.76	46.60	61.76	24.08	2.54	77.20	20.81
3	14.9	641	8.27	258.20	45.40	65.92	26.04	2.45	81.00	20.60
4	15.2	710	8.11	263.49	62.30	75.28	35.51	2.43	71.40	22.14
5	16.2	685	8.20	256.27	63.00	72.86	35.78	2.85	74.60	22.18
6	16.2	693	7.69	253.87	63.70	72.51	34.59	2.20	71.90	21.92
7	17.1	685	7.80	242.81	63.00	76.67	34.99	2.56	73.80	22.26
8	17.2	693	7.79	240.65	64.20	80.83	36.11	2.68	69.20	22.01
9	17.6	688	7.88	235.60	63.70	77.02	35.75	2.71	84.40	22.06
11	18.9	672	8.45	222.62	65.40	81.18	36.23	2.39	71.00	22.35
13	19.2	704	6.92	293.54	54.20	79.45	29.53	2.47	83.70	26.52
14	21.1	725	7.03	294.50	54.40	86.03	30.68	3.14	95.00	29.51
January 2009										
2	10.6	670	7.98	287.05	38.10	91.30	27.69	2.42	83.00	21.54
3	10.5	675	7.95	275.21	39.10	62.98	26.13	2.99	72.30	21.55
4	10.6	729	7.85	293.33	50.80	100.62	32.02	4.16	88.70	21.81
5	9.9	711	7.89	259.99	49.90	89.07	31.62	3.47	74.30	22.05
6	10.2	711	7.93	260.71	48.70	86.09	31.72	4.29	75.10	22.19
7	9.9	693	7.74	247.91	48.10	96.52	31.80	3.19	70.90	22.23
8	9.9	693	7.74	248.63	48.50	76.40	31.54	4.06	71.60	22.89
9	10.0	692	8.12	241.14	50.30	80.87	34.24	4.26	63.40	22.02
11	9.6	665	7.77	235.10	46.10	73.79	34.26	3.35	68.30	22.36
13	15.6	720	7.09	289.71	38.90	98.76	29.96	3.26	74.90	26.95
14	15.7	739	7.68	284.63	40.40	94.66	29.51	3.41	77.80	25.26

TABLE II | Continued

June 2009										
2	14.9	664	8.19	272.38	43.70	62.58	24.40	4.03	76.40	21.89
3										
4	15.0	738	8.14	295.08	61.90	71.68	34.46	4.74	84.80	22.73
5	14.4	722	8.23	273.60	61.90	74.29	34.90	3.37	78.20	23.05
6	14.6	693	8.25	271.40	66.10	67.57	34.66	5.39	79.10	22.87
7										
8	15.7	710	8.23	257.49	66.40	51.52	34.23	4.94	64.30	22.85
9	16.1	691	8.36	252.37	67.30	67.20	34.45	5.28	73.10	22.96
11	16.9	685	8.26	240.41	68.20	78.03	36.11	4.15	71.30	22.91
13	18.5	595	7.67	283.61	58.30	104.16	31.75	5.02	88.00	25.51
14	21.1	612	7.96	293.12	54.30	108.64	31.24	2.92	90.40	28.35